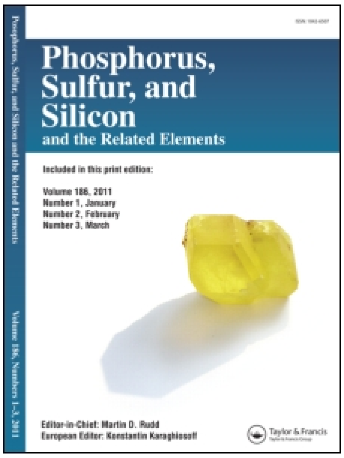

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Heterocyclic Phosphorus Ligands in Coordination Chemistry of Transition Metals

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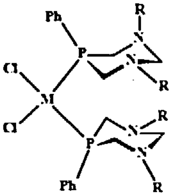
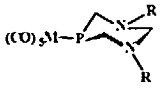
Modern stage of development of organometallic and co-ordination chemistry is characterised by the wide use of polyfunctional ligands with structurally rigid fragments. On the base of such ligands an unusual labile and polynuclear complexes - precursors of the homogeneous catalysts, have been designed. Cyclic organophosphorus compounds pertain to the ligands of such type.

We study the complex formation and structure of transition metal complexes with some novel heterocyclic ligands. Carbonyls of metals of the VI-th group [1] and chlorides of metals of the VIII-th group [2-4] have been chosen as central ions.

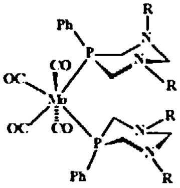
The first studied type of ligands is 1,3,5 – diazaphosphorinanes with one soft (phosphorus) and two hard (nitrogen) donor atoms. Complexes were synthesized by the well-known strategy of ligand exchange. In all cases the formation of metal-phosphorus bond was observed.



M = Pt, Pd



M = W, Mo



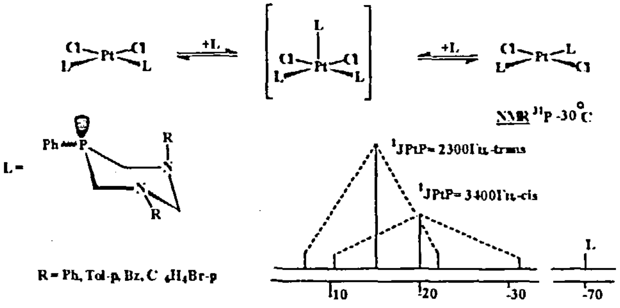
R = Bz, p-Tol, Ph, C_6H_4Br-p

We have compared some spectral characteristics of synthesized complexes (ν_{CO} and $\nu_{M\text{-}Cl}$ in the IR-spectra, $\Delta\delta$ and $^1J_{MP}$ in the NMR ^{31}P spectra) with that of their nearest linear analogues. We have noticed that most of their parameters are close to each other. So the values of Δδ for platinum complexes are subjected to the empirical correlation equation ($\Delta\delta\ ^{31}P = A\delta^{31}P_L + B$, $A=-0.326$, $B=18.83$) established for the linear tertiary phosphines.

Steric volume of ligand, defining by Tolman cone angle, was calculated, on the basis of the X-ray data of free phosphines and their complexes, resting on the new approach, developed by Thomas E.Muller and D.Michael P.Mingos (Transition Met. Chem. 1995, 20, 533).

Crystallographic cone angle, Θ, for 1,3-dibenzyl-5-phenyl-1,3,5-diazaphosphorinane is about 193°. This value is close to that of sterically hindered tertiary phosphines. We managed to isolate and characterise by the X-ray analysis two conformational isomers of platinum complex of 1,3,5-diazaphosphorinane with the different location of MP bonds. The value of Tolman cone angle is greatly changed turning to the conformation with the equatorial location of MP bond. For isomer with axial Pt-P bond - cone angle is 181°, but for isomer with equatorial Pt-P bond, cone angle is 120° (such value is characteristic of the small phosphine ligands). We show by the 1H NMR method that in the solutions of corresponding complexes cyclic ligands mainly exist in chair conformation with the equatorial M-P bond [1].

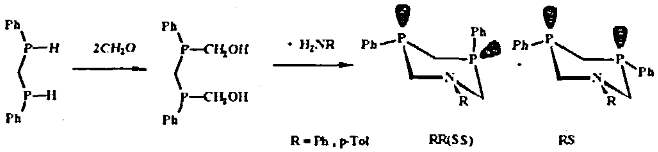
It is well known that small ligands are capable to stabilize unusual high co-ordination numbers of bivalent platinum and palladium. Really, in the presence of additional molecule of ligand in the ^{31}P NMR spectra of L_2PtCl_2 we observed a process of cis-trans isomerisation.



We managed to isolate individual compounds with L_3PtCl_2 composition from these reaction mixtures. One of the complexes gives a mixture of cis-trans isomers and free ligand after dissolving. Probably this compound is an unusually stable intermediate of cis-trans isomerisation. In ^{31}P NMR spectra of another complex we observed signals of three atoms of phosphorus co-ordinated with one atom of metal. At present it is impossible to define exactly whether it is a neutral fivecoordinated platinum complex or ionic square-planar complex [2].

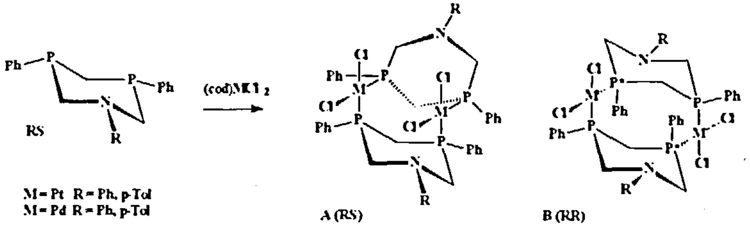
It is well known that phosphines with a hard donor atom in α- position, for example phosphinopyridines, are capable to form fourmembered chelate structures. However we failed to obtain such chelates for 1,3,5-diazaphosphorinanes. We suppose that incorporation of the donor atoms into the cycle greatly limits the possibility of favourable location of their lone pair.

For checking this hypothesis we synthesized the nearest analogue of these ligands, containing two soft phosphorus donor atoms at 1,3-positions of heterocycle [3]. This heterocyclic phosphine exists in two stereoisomeric forms.



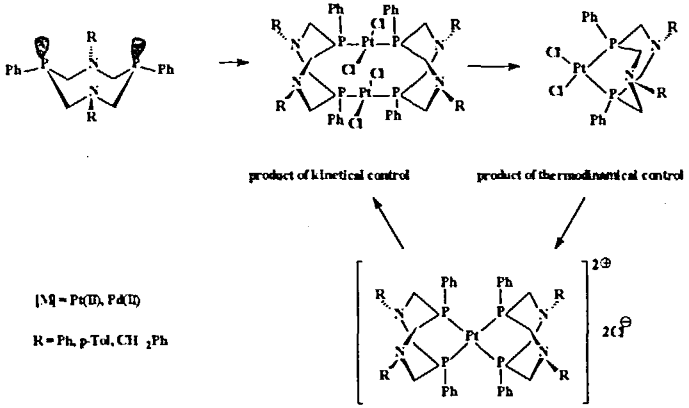
Using fractional crystallisation pure less soluble RS-isomer was isolated. To the best of our knowledge, synthesized heterocycles represent a new class of ligands with two close to each other soft donor atom included to the cycle.

In all conformations of RR(SS) isomer phosphorus lone pair are always orthogonal, but in RS isomer their parallel orientation is possible in chair conformation with di equatorial location of phenyls on phosphorus atoms.



Realization of chelate structures typical for linear diphosphines in these conditions is less probable. Really the synthesized heterocyclic ligands give only binuclear complexes with platinum group metals [3].

In the 1,5,3,7-diazadiphosphacyclooctanes two soft donor phosphorus atoms are situated at the 1,5-positions of more flexible eightmembered heterocycle. We managed to isolate both chelate and binuclear complexes from reaction mixtures [4]. Binuclear complexes convert to the chelate ones in solutions. Probably the first is a product of kinetic, and the second is the product of thermodynamic control.



The X-ray analysis data show that heterocyclic ligands in the chelate complexes exist in chair-boat conformation, while free phosphine exists in crown conformation.

It is necessary to note that chair-boat conformation is typical for all chelate complexes of eightmembered 1,5-donors described in literature. The formation of chelate complex is accompanied by approaching of phosphorus atoms, causing the strain in the cycle. In chair-boat conformation this strain is minimum. In all described structures a significant M-P bond bending, exhibited in 10-20° P-M-P angle distortion is observed [4].

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